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| <p>(54) Title: CATALYST COMPONENTS FOR THE POLYMERIZATION OF DIENES, CATALYST OBTAINED THEREFROM, AND PROCESS FOR THE PREPARATION OF POLYDIENES USING THE SAME</p> <p>(57) Abstract</p> <p>The present invention relates to a catalyst component comprising a compound of a metal selected from the group consisting of Co, Ni and rare earth elements supported on a polymer having a porosity (mercury) higher than 0.02 cm³/g. The use of the above catalyst component makes it possible to prepare dienic polymers, in gas-phase with high yields.</p> | | | |

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**"CATALYST COMPONENTS FOR THE POLYMERIZATION OF DIENES,
CATALYST OBTAINED THEREFROM, AND PROCESS FOR THE PREPARATION
OF POLYDIENES USING THE SAME"**

The present invention relates to a catalyst component for the preparation of polydienes, which is particularly suitable for the use in non-solution processes.

Polydienes polymers are widely known in the art. In particular, butadiene based elastomers, having a high content of cis-1,4 units are extensively used for the production of tires and other elastomeric products.

Generally these products are obtained by solution polymerization using Z/N catalysts based on Titanium, Cobalt, Nickel or rare earth elements. Although allowing the preparation of products of interest, in particular those having a high content of cis-1,4 units, the solution process is not economical since it requires the removal of large quantities of solvent in order to obtain the solid products. Moreover, the productivity of the process cannot reach very high levels because the increase of the concentration of the polymer makes the viscosity of the polymerization medium so high that stirring becomes impossible.

Accordingly, processes more economical and having a lower environment impact, such as gas-phase processes, would be desirable for the preparation of dienic polymers.

In order to have a viable gas-phase process, the catalyst system used must be capable of providing polymers in high yields and with a good (possibly spherical) morphology.

EP-A-647657 discloses a gas-phase process for the polymerization of conjugated dienes using a catalyst component consisting of a rare earth element compound supported on a particular inorganic solid with certain features of surface area and porosity. According to this patent application, the above catalyst component has an activity higher than that of the catalyst component in which the solid inorganic support is absent. However, a still higher activity would be necessary for an economical carry out of a gas-phase process.

WO 96/04322 discloses a gas-phase process for preparation of polydienes carried out under conditions such as to have the diene monomer(s) in the liquid state and in the presence of an inert particulate material. According to said application, the above process should allow to obtain improved yields and reduced polymer fouling. The catalyst system used in said process comprises a metal component of Ni, Co or Ti supported on a porous inorganic support, while carbon black is used as the inert particulate material in the reactor.

In view of the above, it would be desirable to have a gas-phase process for the preparation of

polydienes characterized by easy operability, high productivity and reduction of fouling. In this connection, the term "easy operability" includes avoiding the use of materials in the reactor other than monomers, catalyst system and fluidization gas, and avoiding the use of restrictive polymerization conditions.

We have surprisingly found that by the use of a catalyst system comprising a specific component and a co-catalyst it is possible to carry out a process of this type.

It is therefore an object of the present invention a catalyst component for the polymerization of dienes, comprising a compound of a metal selected from Co, Ni and rare earth elements, supported on a polymer having a porosity, due to pores with a radius up to 100,000 Å, higher than 0.02 cm³/g measured by the mercury method specified below.

Nickel compounds can be selected from organic compounds of nickel with mono- or bidentate organic ligands containing up to 20 carbon atoms. These organonickel compounds are generally soluble in inert solvents. Representative of organonickel compounds are nickel benzoate, nickel acetate, nickel naphthenate, nickel octanoate, nickel neodecanoate, nickel 2-ethylhexanoate, bis(π -allyl nickel), bis(π cycloocta-1,5-diene), bis(π -allyl nickel trifluoroacetate), bis(α -furyl dioxime) nickel, nickel palmitate, nickel stearate, nickel acetylacetone, nickel salicaldehyde, bis(salicylaldehyde) ethylene diimine nickel, bis(cyclopentadiene) nickel, cyclopentadienylnickel nitrosyl and nickel tetracarbonyl. The preferred nickel compounds are selected from nickel salts of carboxylic acids or from nickel organic complexes.

The cobalt compound can be any organic compound such as the cobalt salts of organic acids, cobalt complexes and the like. Preferably, the cobalt compound is selected from the group consisting of cobalt β -ketone complexes, for example, cobalt (II) acetylacetone and cobalt (III) acetylacetone; cobalt β -ketoacid ester complexes, for example, cobalt acetylacetone ethylester complexes; cobalt salts of organic carboxylic acids having 6 or more carbon atoms, for example, cobalt octoate, cobalt naphthenate, and cobalt benzoate; and cobalt halide complexes, for example, cobalt chloride-pyridine complexes; cobalt chloride-ethyl alcohol complexes and cobalt complexes coordinated with butadiene, for example, (1,3-butadiene) [1-(2-methyl-3-butenyl)- π -allyl] -cobalt which may be prepared, for example, by mixing a cobalt compound with an organic aluminum compound, organic lithium compound or alkyl magnesium compound and 1,3-butadiene. Other typical cobalt compounds are cobalt sorbate,

cobalt adipate, cobalt 2-ethylhexoate, cobalt stearate, and the like compounds wherein the organic portion of the molecule contains about 5 to 20, preferably 8 to 18 carbon atoms and one or two carboxylic functions, as well as acetylacetone.

The rare earth metal compounds can be selected from the group consisting of :

- an alcholate of formula $(RO)_3M$ (I);
- a carboxylate of formula $(RCO_2)_3M$ (II);
- a complex compound of the rare earth with diketones and/or an addition compound of the halides of the rare earth with an oxygen or nitrogen donor compound corresponding to the following formulae:
 $(R-CO-CH-CO-R)_3M$ (III)
and
 $ML_3 \bullet y \text{ donor}$ (IV).

In the above formulae M is a trivalent element of the rare earth with atomic numbers of 57 to 71; R groups may be the same or different and represent hydrocarbon radicals containing 1 to 20 carbon atoms; L is chlorine, bromine or iodine; and y is from 1 to 6.

Preferred compounds are those in which M is lanthanum, cerium, praseodymium, gadolinium or neodymium or a mixture of elements of the rare earth which contains at least 10% by weight of at least one of the elements lanthanum, cerium, praseodymium or neodymium. Compounds in which M is lanthanum or neodymium or a mixture of rare earth containing at least 30% by weight of lanthanum or neodymium are most preferred.

The substituents R in formulae (I) to (IV) are, in particular, linear or branched alkyl radicals containing 1 to 15 carbon atoms and preferably 1 to 10 carbon atoms, such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, isopropyl, isobutyl, tert-butyl, 2-ethylhexyl, neopentyl, neoctyl, neodecyl, neododecyl.

Examples of alcoholates of formula (I) are neodymium(III) n-propanolate, neodymium(III) n-butanolate, neodymium(III) n-decanolate, neodymium(III) isopropanolate, neodymium(III) 2-ethylhexanolate, praseodymium(III) n-propanolate, praseodymium(III) n-butanolate, praseodymium(III) n-decanolate, praseodymium(III) isopropanolate, praseodymium(III) 2-ethylhexanolate, lanthanum(III) npropanolate, lanthanum(III) n-butanolate, lanthanum(III) n-decanolate, lanthanum(III) isopropanolate, lanthanum-(III) 2-ethylhexanolate. Preferred compounds are neodymium(III) n-butanolate, neodymium(III) n-decanolate, and neodymium(III) 2-ethylhexanolate.

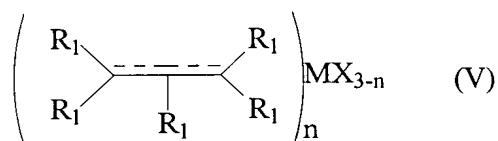
Suitable carboxylates of formula (II) are lanthanum(III) propionate, lanthanum(III) diethyl acetate, lanthanum(III) 2-ethylhexanoate, lanthanum(III) stearate, lanthanum(III) benzoate, lanthanum(III) cyclohexane carboxylate, lanthanum(III) oleate, lanthanum(III) versatate, lanthanum(III) naphthenate, praseodymium(III) propionate, praseodymium(III) diethyl acetate, praseodymium(III) 2-ethylhexanoate, praseodymium(III) stearate, praseodymium(III) benzoate, praseodymium(III) cyclohexane carboxylate, praseodymium(III) oleate, praseodymium(III) versatate, praseodymium(III) naphthenate, neodymium(III) propionate, neodymium(III) diethyl acetate, neodymium(III) 2-ethylhexanoate, neodymium(III) stearate, neodymium(III) benzoate, neodymium(III) cyclohexane carboxylate, neodymium(III) oleate, neodymium(III) versatate, neodymium(III) naphthenate. Preferred compounds are neodymium(III) 2-ethylhexanoate, neodymium(III) versatate, and neodymium(III) naphthenate. Neodymium versatate is particularly preferred.

Suitable complex compounds of formula (III) are lanthanum(III) acetylacetone, praseodymium(III) acetylacetone, neodymium(III) acetylacetone, and preferably neodymium(III) acetylacetone.

Examples of addition compounds of formula (IV) are, for example, lanthanum(III) chloride with tri-butyl phosphate, lanthanum(III) chloride with tetrahydrofuran, lanthanum(III) chloride with isopropanol, lanthanum(III) chloride with pyridine, lanthanum(III) chloride with 2-ethylhexanol, lanthanum(III) chloride with ethanol, praseodymium(III) chloride with tributyl phosphate, praseodymium(III) chloride with tetrahydrofuran, praseodymium(III) chloride with isopropanol, praseodymium(III) chloride with pyridine, praseodymium(III) chloride with 2-ethylhexanol, praseodymium(III) chloride with ethanol, neodymium(III) chloride with tributyl phosphate, neodymium(III) chloride with tetrahydrofuran, neodymium(III) chloride with isopropanol, neodymium(III) chloride with pyridine, neodymium(III) chloride with 2-ethylhexanol, neodymium(III) chloride with ethanol, lanthanum(III) bromide with tri-butyl phosphate, lanthanum(III) bromide with tetrahydrofuran, lanthanum(III) bromide with isopropanol, lanthanum(III) bromide with pyridine, lanthanum(III) bromide with 2-ethylhexanol, lanthanum(III) bromide with ethanol, praseodymium(III) bromide with tributyl phosphate, praseodymium(III) bromide with tetrahydrofuran, praseodymium(III) bromide with isopropanol, praseodymium(III) bromide with pyridine, praseodymium(III) bromide with 2-ethylhexanol, praseodymium(III) bromide with ethanol, neodymium(III) bromide with tributyl phosphate, neodymium(III) bromide with tetrahydrofuran, neodymium(III) bromide with

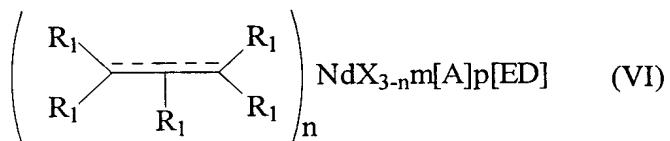
isopropanol, neodymium(III) bromide with pyridine, neodymium(III) bromide with 2-ethylhexanol, neodymium(III) bromide with ethanol. The compounds of the rare earth may be used individually or in admixture with one another.

Another class of compounds usable in the preparation of catalysts for polymerization of dienes is that of the Lanthanide-allyl complexes. These compounds belong to the general formula (V):



where the R_1 groups equal to, or different from, each other are hydrogen or C1-C10 hydrocarbon groups, in particular alkyls; n is 1 or 2; X is selected from halides, carboxylates and alcoholates; and M has the meaning given above.

The complexes in which M is Nd are preferred and, among them, particularly preferred are those of following formula (VI):



where the groups R_1 and n have the same meanings given above, X is Cl or Br, m is an integer from 0 to 2, p is an integer from 0 to 4, A is a salt of a metal belonging to one of the groups from I to IV of the Periodic Table of Elements and ED is an electron donor compound.

The fact that the complexes of the above formula (V) can be found complexed with other molecules is likely a consequence of their preparation methods which often comprise the use of metal-allyl compounds and Nd halides as starting products and certain electron donor compounds as reaction medium. In the above formula (VI) preferred electron donor compounds are ethers and amines, and a preferred metal salts are $MgCl_2$ and $MgBr_2$. When the electron donor is ether it is preferably selected from the group consisting of diethyl ether, dimethoxyethane, tetrahydrofuran (THF) and dioxane.

Examples of usable allyl complexes are Nd(Allyl)₂Cl·1.5THF and Nd(Allyl)Cl₂·2THF whose preparation is described in *Journal of Organometallics Chem.* (1998) 552, pag. 195-204; and the complexes of formula Nd(Allyl)₂Cl·2MgCl₂·4THF (described in *Macromol. Symp.* (1998) 128, pag. 53-61) and Nd(Allyl)₂Cl·MgCl₂·nTHF where n is from 1 to 4. Said complexes, in which also MgCl₂ is present, are generally obtainable by the reaction, in an ether solvent, of a Nd trihalide with a halide of Mg-allyl. Preferably the Nd trihalide is NdCl₃, the ether solvent is tetrahydrofuran and the halide of Mg-allyl is Mg-allyl chloride.

The porous polymer is preferably selected from the group consisting of polyolefin (co)polymers. Preferably it is made up of polyethylene, copolymers of ethylene with proportions less than 20%mol of an olefin selected from propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, cyclohexene, stirene; polypropylene with isotacticity index higher than 80%; crystalline copolymers of propylene with smaller amounts (5% mol or less) of ethylene and/or α -olefins such as 1-butene, 1-hexene.

Said porous polyolefin polymer can be prepared by the polymerization of the monomers carried out in the presence of catalyst comprising the product of the reaction between an organo-Al compound and a solid catalyst component comprising a halide of Ti, Zr, or V supported on a MgCl₂, said solid component having suitable characteristics in terms of porosity and surface area for producing the polymers with the claimed porosity range. Preferably said catalyst components have a spherical form, with particle size from 5 to 200 microns and with surface area (BET) less than 200 m²/g and porosity (mercury method) due to pores with radius up to 10,000 Å, higher than about 0.5 cm³/g and preferably higher than 0.6 cm³/g. Examples of catalyst systems comprising solid components of this type are described for example in EP-A-395083, EP-A-553805, EP-A-553806 and EPA-601525. Said porous polymer can also be in a prepolymerized form that is as a polymer obtained by low conversion polymerization using the catalysts disclosed above. The prepolymer is generally produced in a quantity ranging from 0.5 g per g of solid catalyst component to 2000 g/g. Preferably, however, the amount is between 5 and 500 g per g of solid component and more preferably between 10 and 100 g per g of solid component.

In any case it is essential that the porosity (measured by the mercury method) is higher than 0.02 cm³/g and preferably in the range of from 0.04 to 1.4 cm³/g, more preferably of from 0.04 to 1.2 cm³/g measured by the mercury method described below. In particular when a porous prepolymer is used its porosity is preferably from 0.3 to 1.2 cm³/g, while when a porous

polymer is used its porosity is preferably from 0.04 to 0.3. The porous polymer used in the present invention is further characterized by a porosity, expressed as void percentage, of higher than 10% preferably higher than 15%. In addition, the porous polymer is also preferably endowed with a spherical form that is obtainable for example by using the catalyst components mentioned above.

The metal compound can be supported on said porous polymer using several methods. The term "metal compound supported" used hereafter and hereabove means the metal compound which is not extractable to an extent higher than 50% with heptane at 80°C for 2 hours.

One method comprises the contact of the support and the metal compound in the presence of a liquid medium that is subsequently removed. The so obtained catalyst component is then reacted with the suitable cocatalyst in order to form the final active catalyst.

According to one preferred embodiment instead, the metal compound is first converted into a final active catalyst by suitable reaction with the co-catalyst and then the whole system is supported on the porous polymer. Therefore, this process of supportation specifically comprises:

- (a) suspending the porous polymer in a hydrocarbon medium, preferably propane;
- (b) contacting the so obtained mixture with a hydrocarbon mixture containing the metal component, the cocatalyst and, optionally, a dienic monomer;
- (c) stirring the resulting mixture and finally,
- (d) removing the liquid hydrocarbon medium.

Step (b) is generally carried out working at a temperature between 0 and 100°C, preferably between 10 and 60°C, while step (c) is carried out for time periods ranging from 1 minute to 10 hours. The use of a low boiling point hydrocarbon medium is preferred since it is then possible to remove it simply by flashing. Preferably, before carrying out the step (a) the porous polymer is contacted with an Al-alkyl compound. The use of diisobutylaluminum hydride (DIBAH) is preferred.

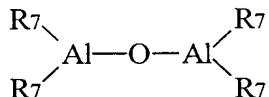
According to another embodiment, the supportation process can be carried out conveniently in a gas-phase loop reactor in which a stream of inert gas keeps the porous polymer moving. The metal compound, optionally dissolved in hydrocarbon solvent, is fed successively, for example using a sprayer, to the gas-phase loop reactor and a smooth-flowing product is obtained at the end of the treatment.

As mentioned above, the active catalysts usable in the polymerization of dienes are formed

upon reaction of the metal components with the suitable cocatalyst compounds.

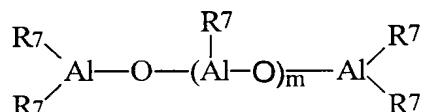
Suitable co-catalysts include organo-Al compounds. In particular, preferred organo-Al compounds are those of formula $\text{AlH}_p\text{R}_q\text{X}_r$ where R is a hydrocarbon group, preferably an alkyl group, having from 1 to 20 carbon atoms, X is halogen, preferably chlorine, p is from 0 to 2, r is from 1 to 3 and q is from 0 to 2. Specific examples are triethylaluminum (TEAL), triisobutylaluminum (TIBA), tris-2,3-dimethylbutylaluminum diethyl aluminum chloride (DEAC), diisobutylaluminum hydride, and partially hydrolyzed diethyl aluminum chloride (DEACO).

Alumoxanes can also be used as cocatalysts in particular when allyl-Lanthanide complexes are used as catalyst components. In particular, the usable alumoxane is considered to be a linear, branched or cyclic compound containing at least one group of the type:

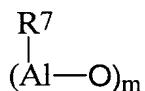


wherein the R^7 substituents, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkylaryl and $\text{C}_7\text{-C}_{20}$ arylalkyl radicals, optionally containing Si or Ge atoms, or R^7 is a group $-\text{O}-\text{Al}(\text{R}^7)_2$.

In particular, linear alumoxanes have formula:



wherein m is an integer ranging from 0 to 40 and R^7 has the meaning reported above; and cyclic alumoxanes have formula:



wherein m is an integer ranging from 2 to 40 and R^7 has the meaning reported above.

In the above-mentioned linear and cyclic alumoxanes, R^7 is preferably methyl, ethyl, isobutyl or 2,4,4-trimethyl-pentyl.

Examples of alumoxanes suitable as activating cocatalysts in the catalyst systems according to the present invention are methylalumoxane (MAO), a modified methylalumoxane obtained by

substituting 20-80% of the methyl groups with a C2 to C12 alkyl group preferably isobutyl (MMAO), isobutylalumoxane (TIBAO) 2,4,4-trimethyl-pentylalumoxane (TIOAO) and 2-methyl-pentylalumoxane. Mixtures of different alumoxanes can also be used.

Suitable activating cocatalysts in the catalyst systems of the invention are also the products of the reaction between water and an organometallic aluminum compound, preferably of formula AlR^7_3 or Al_2R^7_6 , wherein R⁷ has the meaning reported above. Particularly suitable are the organometallic aluminum compounds described in EP 0 575 875 (formula (II)) and those described in WO 96/02580 (formula (II)). Non-limiting examples of organometallic aluminum compounds of formula AlR^7_3 or Al_2R^7_6 are:

tris(methyl)aluminum, tris(isobutyl)aluminum, tris(isooctyl)aluminum
bis(isobutyl-)aluminum hydride, methyl-bis(isobutyl-)aluminum,
dimethyl(isobutyl-)aluminum, tris(isohexyl)aluminum, tris(benzyl)aluminum,
tris(tolyl)aluminum, tris(2,4,4-trimethylpentyl)aluminum,
bis(2,4,4-trimethylpentyl-)aluminum hydride, isobutyl-bis(2-phenyl-propyl)aluminum,
diisobutyl-(2-phenyl-propyl)aluminum, isobutyl-bis(2,4,4-trimethyl-pentyl)aluminum and
diisobutyl-(2,4,4-trimethyl-pentyl)aluminum.

Particularly preferred aluminum compounds are tris(2,4,4-trimethylpentyl)aluminum (TIOA), and triisobutylaluminum (TIBA).

Mixtures of different organometallic aluminum compounds and/or alumoxanes can also be used.

Suitable activating cocatalysts according to the present invention can also be the compounds of formula Y^+Z^- , wherein Y⁺ is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the metal compound, and Z⁻ is a compatible non-coordinating anion, able to stabilize the active catalytic species which results from the reaction of the two compounds and which is sufficiently labile to be displaceable by an olefin substrate. Preferably, the anion Z⁻ consists of one or more boron atoms. More preferably, the anion Z⁻ is an anion of the formula $\text{BAr}_4^{(-)}$, wherein the substituents Ar, the same or different from each other, are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred. Moreover, compounds of the formula BAr_3 can conveniently be used.

When the metal compound is selected from Ni compounds, the cocatalyst is preferably selected from triethylaluminum (TEAL), tris(isobutyl)aluminum (TIBAL) diethylaluminum

chloride (DEAC), MAO and mixtures thereof. Furthermore, also promoters, including hydrogen fluoride, boron trifluoride and their etherate derivatives, are preferably used.

When the metal compound is selected from Co compounds, the cocatalyst is preferably selected from ethylaluminum sesquichloride (EASC), ethylaluminum dichloride (EADC), partially hydrolyzed diethylaluminum chloride (DEACO), MAO and mixtures thereof.

When the metal compound is selected from rare earth metal compounds, the cocatalyst is preferably selected from triethylaluminum (TEAL), tris(isobutyl)aluminum (TIBAL), diisobutylaluminum hydride (DIBAH), MAO and mixtures thereof.

When the catalyst component contains as metal compound the complexes of formulae (V)-(VI) the co-catalyst is preferably MAO.

When the metal compound is selected from those belonging to the formulae (I)-(III) and in particular from Nd carboxylates, the catalyst system is advantageously prepared by reacting the Nd compound with an alkylating agent and with a halogenating agent. The alkylating agent is preferably selected from the trialkyl aluminum compounds like TIBAL, while the halogenating agent is preferably selected from halogenated aluminum alkyls like DEAC or EASC.

Both the Al/Nd and the Cl/Nd molar ratios of the catalyst are somewhat critical for the polymerization activity. Preferably the Al/Nd molar ratio is higher than 10 and more preferably is between 15 and 70. The Cl/Nd molar ratio is preferably higher than 2 and in particular comprised between 2.5 and 5.

It has been observed that when butadiene is to be polymerized the activity of the catalyst system is improved as a consequence of the aging of the catalyst. In particular, aging times higher than 2 days and particularly between 10 and 40 days are suitable to obtain improved very improved yields over the fresh catalyst.

Even the order in which the Nd carboxylate, the alkylating agent and the chlorinating agent are added has an influence on the final properties of the catalyst. Commonly, the catalyst is prepared by first adding the chlorinating agent to the hydrocarbon solution of the Nd carboxylate and then reacting the so obtained slurry mixture with the alkylating agent. In developing this procedure it has been found particularly advantageous, for the increase of the activity, contacting the first mixture with small amounts of the dieninc monomer before adding the alkylating agent.

In the alternative and preferred embodiment, the alkylating agent is firstly added to the

hydrocarbon solution of the Nd carboxylate. The so obtained mixture (first mixture) is then aged for a time longer than 4 hours thereby obtaining a homogeneous mixture which is then added with the halogenating agent. This technique allows to obtain a final catalyst system which is completely soluble in the hydrocarbon medium and that is particularly suitable for the supportation on the porous polymer.

The time span of the aging of the first mixture is preferably about 1 day in particular when carboxylates with at least 10 carbon atoms are used. For the lower carboxylates, longer aging times in particular from about 2 to 10 days are preferred. Generally, the use of longer aging times of the first mixture generates a final catalyst system solution capable to remain clear for times longer than 5 days. Also in this case the aging of the final catalyst solution is beneficial for the activity. In particular, aging times form about 2 to 4 days are especially preferred.

The hydrocarbon medium used for the preparation of the catalyst system is generally selected from the group consisting of saturated hydrocarbons like propane, butane, pentane, hexane, heptane or aromatic hydrocarbons such as toluene and benzene.

As explained above, this catalyst system is particularly suited for the preparation of polydienes by polymerization processes carried out in gas-phase. In particular it is very surprising that, as shown in the following examples, with the use of the polymeric porous support of the invention it is possible to obtain improved yields with respect to those obtainable with the same catalyst system supported on silica as disclosed in the prior art.

The gas-phase process can be carried out in a fluidized bed reactor or under conditions in which the polymer is mechanically stirred, and operating in one or more reactors. The polymerization temperature is generally comprised between -10 and 250°C, preferably between 10 and 160°C. The pressure is generally comprised between 0.1 and 50 bar and preferably between 1 and 20 bar.

The molecular weight of the resulting polymers can be regulated by using molecular weight regulator agents, or by using the polymerization conditions.

As polyene units capable of supplying unsaturated units both conjugated and non-conjugated polyene can be used.

Among conjugated dienes 1,3-butadiene, isoprene, pentadiene or dimethyl butadiene may be used. Straight, non-conjugated dienes can be selected from 1,4-(cis or trans)-hexadiene, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene, alkenyl or alkylidene-norbornenes, such as

5-ethylidene-2-norbornene, 5-isopropylidene-2-norbornene, monocyclic diolefins, such as cis,cis-1,5-cyclooctadiene, 5-methyl-1,5-cyclooctadiene, 4,5,8,9-tetrahydroindene.

As it is known in the art the dienes can also be used in mixtures with other monomers, such as styrene, in order to produce copolymers having specific properties.

The polymers obtained with the catalyst of the invention have a cis-1,4-double bond content of around 60 to 99%. The molecular weight can be adjusted through the composition of the catalyst and by varying the polymerization conditions. Typical molecular weights are in the range from 10^3 to 10^6 , as measured by GPC (gel permeation chromatography).

The Mooney viscosity, ML (1+4', 100°C), is typically in the range from 30 to 180 MU. It is also possible by the gas-phase polymerization to produce polymers of very high molecular weight that would be extremely difficult to obtain by solution polymerization because of the high viscosity and the possibility of transfer reactions through the solvent used.

The polymer obtained may be compounded and vulcanized in the usual way.

The following examples are given in order to better illustrate the invention without limiting it.

EXAMPLES

CHARACTERIZATION

- Effective density: ASTM-D 792.

- Porosity (due to pores with radius up to 100,000Å): the measure is carried out using a "Porosimeter 2000 series" by Carlo Erba.

The porosity is determined by absorption of mercury under pressure. For this determination use is made of a calibrated dilatometer (diameter 3 mm) CD₃ (Carlo Erba) connected to a reservoir of mercury and to a high-vacuum pump ($1 \cdot 10^{-2}$ mba). A weighed amount of sample is placed in the dilatometer. The apparatus is then placed under high vacuum (<0.1 mm Hg) and is maintained in these conditions for 10 minutes. The dilatometer is then connected to the mercury reservoir and the mercury is allowed to flow slowly into it until it reaches the level marked on the dilatometer at a height of 10 cm. The valve that connects the dilatometer to the vacuum pump is closed and then the mercury pressure is gradually increased with nitrogen up to 140 kg/cm². Under the effect of the pressure, the mercury enters the pores and the level goes down according to the porosity of the material.

The porosity (cm³/g), and the distribution of pores is directly calculated from the integral pore distribution curve which is function of the volume reduction of the mercury and applied pressure values (all these data are provided and elaborated by the porosimeter associated

computer which is equipped with a "MILESTONE 200/2.04" program by C. Erba.

The porosity expressed as percentage of voids is calculated from the following formula:

$$X = (100 \cdot V) / V_1$$

where V is the volume of the pores and V_1 is the apparent volume of the sample.

The value of V is directly provided by the instrument that calculates it on the basis of the difference between the initial and final level of the mercury in the. The apparent volume of the sample is given by:

$$V_1 = [P_1 - (P_2 - P)] / D$$

where P is the weight of the sample in grams, P_1 is the weight of the dilatometer+mercury in grams, P_2 is the weight of the dilatometer+mercury+sample in grams and D is the density of mercury (at 25°C = 13.546 g/cm³).

EXAMPLE 1

Supportation of neodium based catalytic system

9.84 grams of a polyethylene pre-polymer having a porosity of 0.341cm³/g were introduced, under nitrogen and at room temperature, into a 250 ml, 2 neck round bottomed flask, that was then connected under nitrogen to a rotavapor. A solution containing 5 mmoles of DIBAH in 10 ml of hexane was added dropwise in 10 minutes. The flask was allowed to rotate for 1 hour at room temperature under nitrogen. The flask was then disconnected from the rotavapor and the solid was dried under reduced pressure for 30 minutes at room temperature, by gently shaking the flask, until a completely free flowing powder was obtained.

Meanwhile, in a 25 ml Schlenk containing a magnetic stirrer, a solution of 0.523 mmoles of Neodium versatate (1.65 ml of a 0.317 M solution in hexane), 0.2 mmoles of isoprene, 15 mmoles of DIBAH (10 mL of a 1.5 M solution in toluene) and 0.3 mmoles of EASC (2.5 ml of a 0.121 M solution in hexane) was prepared.

The solution was stirred for 5 minutes and was then cannulated under nitrogen into the flask and homogeneously distributed on the solid support. The solid was dried at reduced pressure for 30 minutes by gently shaking the flask.

The flask was then weighted and the weight of the supported catalyst was calculated to be 12. 4 grams.

1,3-butadiene polymerization

The flask, containing the supported catalyst prepared as described in the previous paragraph, was connected to the rotavapor and it was allowed to rotate, at 80–100 rpm, plunged in a water

bath thermostatted at 40°C. 1,3-butadiene, previously flashed twice and passed on a column of molecular sieves, was fed into the rotavapor and continuously discharged at a pressure of 0.26 barg.

After 10 minutes, the gas phase polymerization was discontinued by stopping the feeding of 1,3-butadiene and flushing nitrogen through the flask. 22.8 grams of solid were obtained containing 10.4 grams of polybutadiene (activity 99gpol/mmolNd/h/bar).

Comparative example

Supportation of neodium based catalytic system

The same procedure disclosed in Example 1 was followed, except that silica was used instead of the polyethylene pre-polymer as the support for the neodium based catalytic system.

9.24 grams of silica (Grace 955/60) were used as the support, after having been dried at 250°C for 24 hours. 21.04 grams of solid were obtained after the supportation of the catalytic system.

1,3-butadiene polymerization

The polymerization was carried out according to the procedure disclosed in Example 1 with the only difference that the polymerization time lasted 1 hour. At the end of the polymerization 40 grams of solid were recovered corresponding to 18.96 of grams of polybutadiene (activity 30gpol/mmolNd/h/bar).

EXAMPLE 2

Preparation of the homogeneous catalyst solution

A hexane solution containing 0.361mmol of Nd versatate was added with a hexane solution of TIBAL containing 10 mmol of Al. The so obtained solution was left to stand for about one day after which a hexane solution containing 1.08 mmol of DEAC were added. The resulting clear mixture, having a 0.02 molar concentration, was then used in the next step.

Supportation of neodium based catalytic system

15.3 grams of a polypropylene polymer having a porosity of 0.538 cm³/g were introduced, under nitrogen and at room temperature, into a 250 ml, 2 neck round bottomed flask, containing hexane that was then connected under nitrogen to a rotavapor. The homogeneous catalytic solution prepared as disclosed above was then added dropwise in 10 minutes. The flask was allowed to rotate for 30 min. at room temperature under nitrogen. The flask was then disconnected from the rotavapor and the solid was dried under reduced pressure for 30 minutes

at room temperature, by gently shaking the flask, until a completely free flowing powder was obtained containing 0.34% of Nd.

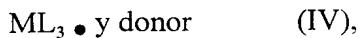
1,3-butadiene polymerization

The flask, containing 7.85 g of the supported catalyst prepared as described in the previous paragraph, was connected to the rotavapor and it was allowed to rotate, at 80–100 rpm, plunged in a water bath at room temperature. 1,3-butadiene, previously flashed twice and passed on a column of molecular sieves, was fed into the rotavapor until a pressure of about 1.2 atmosphere was reached.

After 15 minutes, the gas phase polymerization was discontinued by stopping the feeding of 1,3-butadiene and flushing nitrogen through the flask. 5 grams of polybutadiene were obtained corresponding to an activity of 88gpol/mmolNd/h/bar.

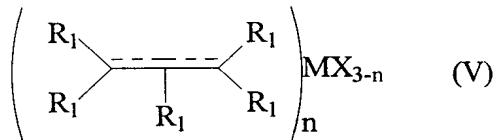
CLAIMS

1. A solid catalyst component for the (co)polymerization of dienes, comprising a compound of a metal selected from Co, Ni and rare earth elements, supported on a polymer having a porosity, due to pores with a radius up to 100.000 Å, higher than 0.02 cm³/g measured by mercury method.
2. A solid catalyst component according to claim 1 in which the porous polymer is selected from the group consisting of polyethylene, copolymers of ethylene with proportions less than 20%mol of an olefin selected from propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, cyclohexene; polypropylene with isotacticity index above 80%; crystalline copolymers of propylene with up to 5% mol of ethylene and/or α -olefins such as 1-butene, 1-hexene.
3. A solid catalyst component according to claim 2 in which the porous polymer is a prepolymer produced in a quantity of from 0.5 to 2000 g per g of solid catalyst component.
4. A solid catalyst component according to claim 3 in which the porous polymer has a porosity in the range of from 0.04 to 1.4 cm³/g measured by the mercury method.
5. A solid catalyst component according to claim 1 in which the porous polymer is further characterized by porosity, expressed as percentage of voids, of higher than 15%.
6. A solid catalyst component according to any of the preceding claims in which the metal compound is selected from compounds of nickel with mono- or bidentate organic ligands containing up to 20 carbon atoms.
7. A solid catalyst component according to any of the claims 1-5 in which the metal compound is selected from cobalt salts of organic acids, or cobalt organic complexes.
8. A solid catalyst component according to any of the claims 1-5 in which the metal compound is selected from rare earth metal compounds belonging to the following classes:
 - an alcholate of formula (RO)₃M (I);
 - a carboxylate of formula (RCO₂)₃M (II);
 - complex compound of the rare earth with diketones and/or an addition compound of the halides of the rare earth with an oxygen or nitrogen donor compound corresponding to the formulae
$$(R-CO-CH-CO-R)_3M \text{ (III)}$$
and



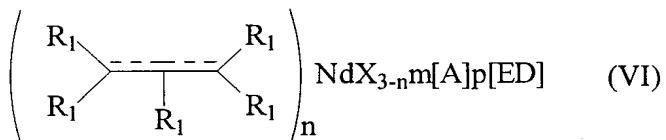
where M is a trivalent element of the rare earth with atomic numbers of 57 to 71; R groups may be the same or different and represent hydrocarbon radicals containing 1 to 10 carbon atoms; L is chlorine, bromine or iodine; and y is from 1 to 6.

9. A solid catalyst component according to claim 8 in which the metal compound is selected from those of formula (II) in which M is neodymium and in which the substituents R are linear or branched alkyl radicals containing 1 to 10 carbon atoms.
10. A solid catalyst component according to claim 9 in which the carboxylates are selected from the group consisting neodymium(III) 2-ethylhexanoate, neodymium(III) versatate and neodymium(III) naphthenate.
11. A solid catalyst component according to any of the claims 1-5 in which the metal compound is selected from rare earth metal compounds of formula (V):



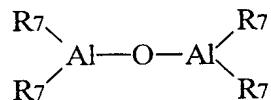
where the R₁ groups equal to, or different from, each other are hydrogen or C1-C10 hydrocarbon groups, in particular alkyls; n is 1 or 2; X is selected from halides, carboxylates and alcoholates; and M has the meaning given above.

12. A solid catalyst component according to claim 11 in which M is Nd.
13. A solid catalyst component according to claim 12 in which the Nd compound is selected from those of the following formula (VI):



where the groups R1 and n has the same meanings given above, X is Cl or Br, m is an integer from 0 to 2, p is an integer from 0 to 4, A is a salt of a metal belonging to one of the groups from I to IV of the Periodic Table of Elements and ED is an electron donor compound.

14. A solid catalyst component according to claim 13 in which electron donor compound is selected from ethers and amines, and the metal salt is MgCl₂ or MgBr₂.
15. A solid catalyst component according to claim 14 in which the electron donor is ether selected from the group consisting of diethyl ether dimethoxyethane, tetrahydrofuran (THF) and dioxane.
16. Catalyst for the (co)polymerization of dienes comprising the reaction product of a solid catalyst component according to any of the preceding claims with a co-catalyst.
17. Catalyst according to claim 16 in which the cocatalyst is selected from the group consisting of:
 - organo-Al compounds of formula AlH_pR_qX_r where R is a hydrocarbon group, preferably an alkyl group, having from 1 to 20 carbon atoms, X is halogen, preferably chlorine, p is from 0 to 2, r is from 1 to 3 and q is from 0 to 2;
 - alumoxanes containing at least one group of the type:



- wherein the R⁷ substituents, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl and C₇-C₂₀-aryl-alkyl radicals, optionally containing Si or Ge atoms, or R⁷ is a group -O-Al(R⁷)₂;
- compounds of formula Y⁺Z⁻, wherein Y⁺ is a Broensted acid, able to donate a proton and to react irreversibly with a substituent X of the metal compound, and Z⁻ is a compatible non-coordinating anion, able to stabilize the active catalytic species which results from the reaction of the two compounds and which is sufficiently labile to be displaceable by an olefin substrate.

18. Catalyst for the (co)polymerization of dienes comprising the reaction product of a solid catalyst component according to claim 6 and a cocatalyst selected from the group consisting of triethylaluminum (TEAL), tris(isobutyl)aluminum (TIBAL) diethylaluminum chloride (DEAC), MAO and mixtures thereof.
19. Catalyst for the (co)polymerization of dienes comprising the reaction product of a solid catalyst component according to claim 7 and a cocatalyst selected from the group consisting of ethylaluminum sesquichloride (EASC), ethylaluminum dichloride (EADC),

- partially hydrolyzed diethylaluminum chloride (DEACO), MAO and mixtures thereof.
20. Catalyst for the (co)polymerization of dienes comprising the product of the reaction between a solid catalyst component according to any of the claims 8-10 and an alkylating agent and with a halogenating agent.
 21. Catalyst according to claim 26 in which the alkylating agent is selected from the trialkyl aluminum compounds and the halogenating agent is selected from halogenated aluminum alkyls.
 22. Catalyst for the (co)polymerization of dienes comprising the product of the reaction of
 - (a) a porous polymer having a porosity, due to pores with a radius up to 100.000 Å, higher than 0.02 cm³/g measured by mercury method; and
 - (b) the product of the reaction between (i) a rare earth metal compound belonging to one of the formulae (I)-(III) of claim 12; (ii) an alkylating agent; and (iii) a halogenating agent, said components (i)-(iii) being reacted in a hydrocarbon medium.
 23. Catalyst according to claim 22 in which the alkylating agent is selected from the trialkyl aluminum compounds and the halogenating agent is selected from chlorinated aluminum alkyls.
 24. Catalyst according to claim 23 in which the rare earth metal of formulae (I)-(III) is Nd; the Al/Nd molar ratio is between 30 and 70 and the Cl/Nd molar ratio is between 2.5 and 6.
 25. Catalyst according to claim 28 in which the reaction product (b) is aged for a period longer than 2 days.
 26. Catalyst according to claim 23 in which the component (b) is obtained by reacting the component (iii) with a mixture, obtained by contacting the components (i) and (ii), which has been aged for a period longer than 4 hours.
 27. Catalyst according to claim 26 in which the mixture obtained by contacting the components (i) and (ii) is aged for a period longer than 1 day.
 28. Process for the preparation of a catalyst component according to claims 1-15 comprising contacting, a compound of a metal selected from Co, Ni and rare earth elements, with a polymer having a porosity, due to pores with a radius up to 100.000 Å, higher than 0.02 cm³/g measured by mercury method.
 29. Process according to claim 28 in which the contact is carried out in a liquid hydrocarbon medium.
 30. Process according to claim 28 in which the contact is carried out in gas-phase.

31. Process for the (co)polymerization of dienes characterized in that it is carried out in the presence of a catalyst system according one or more of the claims 16-27.
32. Process according to claim 31 characterized in that the process is carried out in gas phase.
33. Process according to claim 26 in which the diene is selected from the group consisting of 1,3-butadiene, isoprene, pentadiene or dimethyl butadiene, 1,4-(cis or trans)-hexadiene, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene, 5-ethylidene-2-norbornene, 5-isopropylidene-2-norbornene cis,cis-1,5-cyclooctadiene, 5-methyl-1,5-cyclooctadiene, 4,5,8,9-tetrahydroindene.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/06979

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|-------------------------------------|-----------|----------|----------|----------|
| A. CLASSIFICATION OF SUBJECT MATTER | | | | |
| IPC 7 | C08F36/04 | C08F4/02 | C08F4/70 | C08F4/54 |

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|----------------------------------|
| P, X | EP 0 903 355 A (BAYER AG) 24 March 1999 (1999-03-24) page 3, lines 31-35 and 49-56 claims; examples ---- | 1-33 |
| P, X | DE 197 54 789 A (BAYER AG) 1 July 1999 (1999-07-01) page 2, line 27 - line 31; claims; examples ---- | 1-5, 8-13, 16-27, 31-33 |
| X | WO 96 04322 A (CANN KEVIN JOSEPH ;WILLIAMS GARY HARRY (US); APECETCHE MARIA ANGEL) 15 February 1996 (1996-02-15) cited in the application page 10, line 29 - line 30; claims 1,7 ---- -/-- | 1,2,6,7, 16-19, 30-32 |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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| Date of the actual completion of the international search | Date of mailing of the international search report |
| 13 January 2000 | 24/01/2000 |
| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Authorized officer Van Humbeeck, F |

INTERNATIONAL SEARCH REPORT

Inte onal Application No

PCT/EP 99/06979

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-----------------------|
| A | WO 95 10542 A (EXXON CHEMICAL PATENTS INC) 20 April 1995 (1995-04-20) page 6, line 15; claim 6 ----- | 1 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/06979

| Patent document cited in search report | | Publication date | Patent family member(s) | | Publication date |
|--|---|------------------|-------------------------|-------------|------------------|
| EP 0903355 | A | 24-03-1999 | JP | 11158208 A | 15-06-1999 |
| DE 19754789 | A | 01-07-1999 | | NONE | |
| WO 9604322 | A | 15-02-1996 | US | 5453471 A | 26-09-1995 |
| | | | AT | 184886 T | 15-10-1999 |
| | | | AU | 691957 B | 28-05-1998 |
| | | | AU | 3211395 A | 04-03-1996 |
| | | | AU | 687604 B | 26-02-1998 |
| | | | AU | 3211495 A | 04-03-1996 |
| | | | AU | 692586 B | 11-06-1998 |
| | | | AU | 3237395 A | 04-03-1996 |
| | | | BR | 9503534 A | 16-04-1996 |
| | | | BR | 9508515 A | 21-10-1997 |
| | | | BR | 9508517 A | 21-10-1997 |
| | | | CA | 2155236 A,C | 03-02-1996 |
| | | | CA | 2196664 A | 15-02-1996 |
| | | | CN | 1133298 A | 16-10-1996 |
| | | | CN | 1158624 A | 03-09-1997 |
| | | | CN | 1171793 A | 28-01-1998 |
| | | | CZ | 9700296 A | 11-06-1997 |
| | | | CZ | 9700297 A | 11-06-1997 |
| | | | CZ | 9700320 A | 11-06-1997 |
| | | | DE | 69512421 D | 28-10-1999 |
| | | | EP | 0697421 A | 21-02-1996 |
| | | | EP | 0773964 A | 21-05-1997 |
| | | | EP | 0773963 A | 21-05-1997 |
| | | | EP | 0773965 A | 21-05-1997 |
| | | | EP | 0856531 A | 05-08-1998 |
| | | | EP | 0856530 A | 05-08-1998 |
| | | | FI | 970457 A | 18-04-1997 |
| | | | HU | 78022 A | 28-05-1999 |
| | | | HU | 78018 A | 28-05-1999 |
| | | | HU | 76682 A | 28-10-1997 |
| | | | JP | 8100009 A | 16-04-1996 |
| | | | JP | 10503799 T | 07-04-1998 |
| | | | JP | 10503800 T | 07-04-1998 |
| | | | NO | 970464 A | 21-03-1997 |
| | | | PL | 318524 A | 23-06-1997 |
| | | | PL | 318526 A | 23-06-1997 |
| | | | PL | 318527 A | 23-06-1997 |
| | | | SK | 14897 A | 10-09-1997 |
| | | | WO | 9604323 A | 15-02-1996 |
| | | | WO | 9604321 A | 15-02-1996 |
| | | | US | 5834571 A | 10-11-1998 |
| | | | ZA | 9506456 A | 14-03-1996 |
| WO 9510542 | A | 20-04-1995 | US | 5466649 A | 14-11-1995 |
| | | | DE | 69421287 D | 25-11-1999 |
| | | | EP | 0723557 A | 31-07-1996 |
| | | | US | 5516737 A | 14-05-1996 |
| | | | US | 5516861 A | 14-05-1996 |

DERWENT-ACC-NO: 2000-338879**DERWENT-WEEK:** 200267

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TITLE: Solid diene polymerization catalyst,
comprises transition metal compound on
porous polymer**INVENTOR:** FUSCO O; GALIMBERTI M ; GIOIA G**PATENT-ASSIGNEE:** BASELL TECHNOLOGY CO BV[BASE] ,
MONTELL TECHNOLOGY CO BV[MONT]**PRIORITY-DATA:** 1998EP-203313 (September 26, 1998)**PATENT-FAMILY:**

| PUB-NO | PUB-DATE | LANGUAGE |
|------------------|-------------------|-----------------|
| WO 0018812 A1 | April 6, 2000 | EN |
| AU 9961937 A | April 17, 2000 | EN |
| EP 1032603 A1 | September 6, 2000 | EN |
| ZA 200002583 A | April 25, 2001 | EN |
| BR 9913013 A | May 2, 2001 | PT |
| CN 1286703 A | March 7, 2001 | ZH |
| HU 200004951 A2 | May 28, 2001 | HU |
| KR 2001032176 A | April 16, 2001 | KO |
| MX 2000005189 A1 | September 1, 2001 | ES |
| JP 2002525402 W | August 13, 2002 | JA |

DESIGNATED-STATES: AU BR CA CN HU IL IN JP KR MX RU SG
US ZA AT BE CH CY DE DK ES FI FR GB
GR IE IT LU MC NL PT SE AT BE CH CY
DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

APPLICATION-DATA:

| PUB-NO | APPL- DESCRIPTOR | APPL-NO | APPL-DATE |
|----------------|-----------------------------|----------------|--------------------|
| WO2000018812A1 | N/A | 1999WO-EP06979 | September 21, 1999 |
| AU 9961937A | N/A | 1999AU-061937 | September 21, 1999 |
| BR 9913013A | N/A | 1999BR-013013 | September 21, 1999 |
| CN 1286703A | N/A | 1999CN-801670 | September 21, 1999 |
| EP 1032603A1 | N/A | 1999EP-948809 | September 21, 1999 |
| EP 1032603A1 | N/A | 1999WO-EP06979 | September 21, 1999 |
| BR 9913013A | N/A | 1999WO-EP06979 | September 21, 1999 |
| HU 200004951A2 | N/A | 1999WO-EP06979 | September 21, 1999 |
| JP2002525402W | N/A | 1999WO-EP06979 | September 21, 1999 |
| HU 200004951A2 | N/A | 2000HU-004951 | September 21, 1999 |
| JP2002525402W | N/A | 2000JP-572270 | September 21, 1999 |
| KR2001032176A | N/A | 2000KR-705364 | May 17, 2000 |
| ZA 200002583A | N/A | 2000ZA-002583 | May 24, 2000 |
| MX2000005189A1 | Based on | 2000MX-005189 | May 25, 2000 |

INT-CL-CURRENT:

| TYPE | IPC DATE |
|-------------|--------------------|
| CIPS | C08F36/02 20060101 |

| | |
|------|--------------------|
| CIPS | C08F36/04 20060101 |
| CIPS | C08F4/02 20060101 |
| CIPS | C08F4/54 20060101 |
| CIPS | C08F4/602 20060101 |
| CIPS | C08F4/70 20060101 |

ABSTRACTED-PUB-NO: WO 0018812 A1

BASIC-ABSTRACT:

NOVELTY - Solid diene polymerization catalyst, comprises a cobalt, nickel or rare earth metal compound, supported on a polymer. The polymer has more than 0.02 cm³/g (measured by mercury method) pores with radius at most 100000 Angstrom.

USE - Diene polymers are used in non-solution processes, particularly for the production of tires and other elastomeric products.

ADVANTAGE - The catalyst has improved yields, and has easy operability, high productivity and reduced fouling.

EQUIVALENT-ABSTRACTS:

POLYMERS

Preferred Porous Polymer: The porous polymer comprises polyethylene, copolymer of ethylene with less than 20 mol % olefin including propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene or cyclohexene, polypropylene with isotacticity index more than 80%, or crystalline copolymer of propylene with at most 5 mol% ethylene and/or alpha-olefin, e.g., 1-butene or 1-hexene. It may be a prepolymer produced in 0.5-2000 g/g solid catalyst component. It has a porosity = 0.04-1.4 cm³/g or more than 15% of voids.

Preferred Dienes: The diene includes 1,3-butadiene, isoprene, pentadiene or dimethyl butadiene, 1,4-(cis or trans)- hexadiene, 6-methyl- 1,5-heptadiene, 3,7-dimethyl- 1,6-octadiene, 5-ethylidene- 2-norbornene, 5-isopropylidene- 2-norbornene, cis,cis-1,5-cyclooctadiene, 5-methyl- 1,5-cyclooctadiene or 4,5,8,9-tetrahydroindene.

ORGANIC CHEMISTRY

Preferred Compound: The metal compound comprises a complex of nickel and 20 C mono or bidentate organic ligands, an alcoholate rare earth metal compound of formula (I), a carboxylate rare earth metal compound of formula (II), a complex of the rare earth with diketone, and/or an addition compound of the halide of the rare earth with an oxygen or nitrogen donor compound of formula (III) and/or (IV).

(RO)₃M (I)

(RCO₂)₃M (II)

(R-CO-CH-CO-R)₃M (III)

ML₃y (IV)

M = trivalent element of the rare earth with atomic number = 57-71 (sic)

R = 1-10 C hydrocarbon radical

L = chlorine, bromine or iodine

y = 1-6

Carboxylate includes neodymium (III) 2-ethylhexanoate, neodymium (III) versenate or neodymium (III) naphthenate. The metal compound may be rare earth metal compounds of formula (V).

R₁ = H or 1-10 C hydrocarbon particularly alkyl

n = 1 or 2

X = halide, carboxylate or alcoholate

The neodymium compound includes compounds of formula (VI).

X = Cl or Br

m = 0-2

p = 0-4

A = salt of a group I-IV metal

ED = electron donor

The electron donor compound includes ether or amine. It may also include diethyl ether dimethoxyethane, tetrahydrofuran (THF) or dioxane.

Preferred Catalyst: The catalyst has a cocatalyst. The cocatalyst includes ethylaluminum sesquichloride (EASC), ethylaluminum dichloride (EADC), partially hydrolyzed diethylaluminum chloride (DEACO) and/or MAO, and optionally triethylaluminum (TEAL), tris(isobutyl) aluminum (TIBAL), diethylaluminum chloride and/or MAO.

The cocatalyst may include organo-aluminum compounds of formula (VII), alumoxane containing group of formula (VIII) or compounds of formula (IX).

Al_{HP}R_qX_r (VII)

Al(R₇)₂-O-Al(R₇)₂ (VIII)

Y+Z- (IX)

R = 1-20 C hydrocarbon, preferably alkyl

X = halogen, preferably Cl

p = 0-2

r = 1-3

q = 0-2

R7 = H, linear or branched (un)saturated 1-20 C alkyl, 3-20 C cycloalkyl, 6-20 C aryl, 7-20 C alkylaryl or 7-20 C aryl-alkyl radical, optionally containing Si or Ge, group of formula (X)

Y+ = Bronsted acid, able to donate a proton and to react irreversibly with a substituent X of the metal compound

Z- = compatible non-coordinating anion, able to stabilize the active species which results from the reaction of the two compounds and which is labile to be displaceable by an olefin substrate

-O-Al(R7)2 (X)

The catalyst is the reaction product of a solid catalyst component and an alkylating agent, and with a halogenating agent. The alkylating agent includes trialkyl aluminum compound, and the halogenating agent includes halogenated, preferably chlorinated aluminum alkyl. The catalyst may comprise the product of the reaction of a porous polymer and the product of the reaction (in a hydrocarbon medium) between:

(i) a rare earth metal compound of the formula (I), (II) or (III),

(ii) an alkylating agent, and

(iii) a halogenating agent.

INORGANIC CHEMISTRY

Preferred Process: The contacting step is carried out in a liquid hydrocarbon medium and/or in gas phase. The reaction product is aged for more than 2 days.

5 mmols DIBAH in 10 ml hexane was added to 9.84 g polyethylene prepolymer with a porosity = 0.341 cm³/g, rotated and dried to give a free flowing powder. A solution of 0.523 mmoles neodymium versatate, 0.2 mmoles isoprene, 15 mmoles DIBAH, and 0.3 mmoles EASC was cannulated and homogeneously distributed on the solid support. The solid was dried. The supported catalyst weighed 12.4 g.

1,3-butadiene was fed and continuously discharged at 0.26 bar g (40 degrees C). After 10 minutes, the gas phase polymerization stopped. 22.8 g solid containing 10.4 g polybutadiene with an activity of 99 g polymer/mmol Nd/hour/bar was obtained.

TITLE-TERMS: SOLID DIENE CATALYST COMPRISE TRANSITION METAL COMPOUND POROUS POLYMER

DERWENT-CLASS: A12 E12

CPI-CODES: A02-A06; A02-D; A04-B01A; A04-G01E; A12-W11K; E05-L02B; E05-L02C; E05-P;

CHEMICAL-CODES: Chemical Indexing M3 *01* Fragmentation Code A428 A960 C710 J5 J582 M210 M211 M262 M282 M311 M321 M342 M382 M391 M411 M510 M520 M530 M540 M620 M630 M781 Q121 R032 R044 Specific Compounds R13110 RAOLRE Registry Numbers 129603 129605 129632 129682 129962 129963 130527 130929 132574 132685 132820 132834 132936 133227 134705 135140 188089 190866 300 429 562 679 721

Chemical Indexing M3 *02* Fragmentation

Code A427 A960 C710 J5 J582 M210 M211
M262 M282 M311 M321 M342 M382 M391 M411
M510 M520 M530 M540 M620 M630 M781 Q121
R032 R044 Specific Compounds R05096
Registry Numbers 129603 129605 129632
129682 129962 129963 130527 130929
132574 132685 132820 132834 132936
133227 134705 135140 188089 190866 300
562 679 721

Chemical Indexing M3 *03* Fragmentation
Code A428 A960 C710 G030 G033 G034 G035
G036 G037 G553 G563 J0 J011 J012 J1
J151 J152 M210 M211 M212 M213 M214 M231
M232 M233 M240 M281 M282 M283 M320 M411
M510 M520 M530 M541 M630 M781 Q121 R032
R044 Specific Compounds R13139 Registry
Numbers 133840 133899 133900 133902
133903 133904 133907 134163 189794
190895

Chemical Indexing M3 *04* Fragmentation
Code A428 A923 C720 G030 G581 M280 M320
M411 M510 M520 M530 M541 M640 M781 Q121
R032 R044 Ring Index Numbers 00417
Specific Compounds RA0M4C Registry
Numbers 435

Chemical Indexing M3 *05* Fragmentation
Code A428 A923 G030 G039 G551 G599 M1
M126 M144 M280 M320 M411 M510 M520 M530
M542 M781 Q121 R032 R044 Specific
Compounds RA0QBC Registry Numbers 2822

Chemical Indexing M3 *06* Fragmentation
Code A760 A960 C710 G033 G034 G035 G036
G037 G553 G563 J0 J011 J012 J1 J151
J152 M210 M211 M212 M213 M214 M231 M232
M233 M240 M281 M282 M283 M320 M411 M510
M520 M530 M541 M630 M781 Q121 R032 R044
Specific Compounds RA163L Registry

Numbers 255967

Chemical Indexing M3 *07* Fragmentation
Code A760 A960 C710 J0 J011 J1 J171
M220 M223 M232 M233 M262 M281 M320 M411
M510 M520 M530 M540 M620 M630 M781 Q121
R032 R044 Specific Compounds RA0WDY
Registry Numbers 243221

Chemical Indexing M3 *08* Fragmentation
Code A760 A960 C710 J0 J011 J1 J171
M220 M221 M232 M262 M281 M320 M411 M510
M520 M530 M540 M620 M630 M781 Q121 R032
R044 Specific Compounds RA1SC5 Registry
Numbers 285867

Chemical Indexing M3 *09* Fragmentation
Code A428 A960 C710 G003 G010 G020 G021
G030 G040 G050 G100 G221 G553 G563 H607
H685 J0 J011 J1 J131 J151 J171 M210
M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233
M240 M262 M280 M281 M311 M320 M321 M344
M349 M362 M391 M411 M510 M520 M530 M531
M540 M541 M620 M630 M781 Q121 R032 R044
Markush Compounds 001681901

Chemical Indexing M3 *10* Fragmentation
Code A427 A960 C710 G010 G020 G021 G030
G040 G050 G100 G221 G553 G563 J0 J011
J012 J1 J131 J151 J171 J172 M210 M211
M212 M213 M214 M215 M216 M220 M221 M222
M223 M224 M225 M226 M231 M232 M233 M262
M280 M281 M311 M312 M313 M314 M315 M316
M320 M321 M331 M332 M333 M340 M342 M382
M391 M411 M510 M520 M530 M531 M540 M541
M620 M630 M781 Q121 R032 R044 Markush
Compounds 001681902

Chemical Indexing M3 *11* Fragmentation
Code A427 A960 C710 C801 C802 C803 C804

C805 C806 C807 J011 J271 J5 J581 J582
M210 M211 M212 M213 M214 M215 M216 M220
M221 M222 M223 M224 M225 M226 M231 M232
M233 M262 M272 M281 M282 M311 M321 M342
M382 M391 M411 M510 M520 M530 M540 M620
M630 M650 M781 Q121 R032 R044 Markush
Compounds 001681903

Chemical Indexing M3 *12* Fragmentation
Code A657 A700 A758 A759 A760 A960 C710
C801 C802 C803 C804 C805 C806 C807 G003
G010 G020 G021 G030 G040 G050 G100 G221
G553 G563 J0 J011 J1 J131 J151 J171
M210 M211 M212 M213 M214 M215 M216 M220
M221 M222 M223 M224 M225 M226 M231 M232
M233 M240 M262 M280 M281 M320 M411 M510
M520 M530 M531 M540 M541 M620 M630 M781
Q121 R032 R044 Markush Compounds
001681904

Chemical Indexing M3 *13* Fragmentation
Code A657 A700 A758 A759 A760 A960 C710
C801 C802 C803 C804 C805 C806 C807 G003
G010 G020 G021 G030 G040 G050 G100 G221
G553 G563 H4 H401 H441 H461 H481 H8
M210 M211 M212 M213 M214 M215 M216 M220
M221 M222 M223 M224 M225 M226 M231 M232
M233 M240 M272 M280 M281 M320 M411 M510
M520 M530 M531 M540 M541 M620 M630 M781
Q121 R032 R044 Markush Compounds
001681905

Chemical Indexing M3 *14* Fragmentation
Code A700 A960 C710 C801 C802 C803 C804
C805 C806 C807 J011 J271 J5 J581 J582
M210 M211 M212 M213 M214 M215 M216 M220
M221 M222 M223 M224 M225 M226 M231 M232
M233 M262 M272 M281 M282 M311 M321 M342
M382 M391 M411 M510 M520 M530 M540 M620
M630 M650 M781 Q121 R032 R044 Markush
Compounds 001681906

Chemical Indexing M3 *15* Fragmentation
Code A760 A910 A923 A940 A960 C000 C100
C710 C720 C801 C802 C803 C804 C805 C806
C807 H401 H481 J011 J171 M210 M211 M212
M213 M214 M215 M216 M220 M221 M222 M223
M224 M225 M226 M231 M232 M233 M262 M272
M280 M281 M320 M411 M510 M520 M530 M540
M620 M630 M640 M781 Q121 R032 R044
Markush Compounds 001681907

**UNLINKED-DERWENT-REGISTRY-
NUMBERS:**

; 1047U ; 1537U

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]
018 ; G0817*R D01 D51
D54 G0839 G0828 G0817
D12 D10 D56 G0942 G0931
D02 D57 G0920 G0917 D13
D14 D16 D31 D32 D77 D58
D59 D86 D85 D87 D90 D88
D89; G0828 G0817 D01 D02
D12 D10 D51 D54 D56 D58
D84 R00806 129411; G0828
G0817 D01 D02 D12 D10
D51 D54 D56 D58 D85
R00429 483; G0828 G0817
D01 D02 D12 D10 D51 D54
D56 D58 D59 D85 R01299
1249; G0931 G0817 D01
D02 D12 D10 D51 D54 D57
D58 D59 D86 R01402
129412; G0917 G0817 D01
D02 D05 D12 D10 D16 D13
D32 D51 D54 D57 D59 D77
D89 R01608 129408;
H0000; H0022 H0011;
H0033 H0011; L9999 L2573
L2506; L9999 L2528
L2506; L9999 L2562
L2506; H0124*R; P0328;
P0339;

Polymer Index [1.2]
018 ; ND02; Q9999
Q9256*R Q9212;

Polymer Index [1.3]
018 ; C999 C168; C999
C293; S9999 S1456*R;
B9999 B5221 B4740;

Polymer Index [1.4]
018 ; Co 8B Tr Ni 9A*R
Nd 9A Cl 7A Br I* D01
D11 D10 D12 D50 D61*R
D68 D70 D81 D82 D83 D84
D85 D86 D87 D88 D89 D90
D91 D92 D93 D94 D95 F23
F36 F35 F37 F38 N* 5A
1A*R 2A*R 3A*R 4A*R D00
Mg 2A; D00 D70 Mg 2A Cl
7A R01801 99995; C999
C000*R; C999 C033 C000;
C999 C293; C999 C248;

Polymer Index [1.5]
018 ; D01 D11 D10 D50
D87 F34 F07*R; G1592 D01
D23 D22 D31 D42 D50 D75
D84 F34 R00895 19; G1592
D01 D23 D22 D31 D46 D50
D76 D84 F34 R01057 30;
C999 C135 C113; C999
C293;

Polymer Index [1.6]
018 ; D01 D11 D10 D50
D68 D70 D81 D82 D83 D84
D85 D86 D87 D88 D89 D90
D91 D92 D93 D94 D95 Al
3A 7A*R O* 6A Si 4A Ge
D13*R D12 D18*R D51*R;
D01 D11 D10 D50 D68 D86

Al 3A R00659 351; D01
D11 D10 D50 D68 D92 A1
3A R00728 215; D01 D11
D10 D50 D68 D70 D84 A1
3A C1 7A R00639 643; D01
D11 D10 D50 D68 D70 D86
A1 3A C1 7A R05194
135342; D01 D11 D10 D50
D68 D70 D82 A1 3A C1 7A
R01381 1158; C999 C124
C113; C999 C293; C999
C340;

Polymer Index [2.1]
018 ; H0000; G0044 G0033
G0022 D01 D02 D12 D10
D51 D53 D58 D82 R00326
1013; C999 C168; S9999
S1456*R; H0259; P1150;
P1161;

Polymer Index [2.2]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D82
R00326 1013; G0033*R
G0022 D01 D02 D51 D53
G0099 G0088 G0033 D13
D14 D31 D75 D76 D59;
C999 C168; S9999
S1456*R; H0259; P1150;

Polymer Index [2.3]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D82
R00326 1013; G0044 G0033
G0022 D01 D02 D12 D10
D51 D53 D58 D83 R00964
1145; C999 C168; S9999
S1456*R; H0259; P1150;

P1285;

Polymer Index [2.4]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D82
R00326 1013; G0055 G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D84
R00805 11179; C999 C168;
S9999 S1456*R; H0259;
P1150; P1263;

Polymer Index [2.5]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D82
R00326 1013; G0044 G0033
G0022 D01 D02 D12 D10
D51 D53 D58 D86 R02043
785; C999 C168; S9999
S1456*R; H0259; P1150;

Polymer Index [2.6]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D82
R00326 1013; G0044 G0033
G0022 D01 D02 D12 D10
D53 D51 D58 D86 R15485
53813; C999 C168; S9999
S1456*R; H0259; P1150;

Polymer Index [2.7]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D82
R00326 1013; G0044 G0033
G0022 D01 D02 D12 D10
D51 D53 D58 D88 R00936
251; C999 C168; S9999

S1456*R; H0259; P1150;

Polymer Index [2.8]
018 ; H0000; G0044 G0033
G0022 D01 D02 D12 D10
D51 D53 D58 D83 R00964
1145; C999 C124 C113;
S9999 S1456*R; H0259;
P1150; P1343;

Polymer Index [2.9]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D83
R00964 1145; G0033*R
G0022 D01 D02 D51 D53
H0215; C999 C124 C113;
S9999 S1456*R; H0259;
P1150;

Polymer Index [2.10]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D83
R00964 1145; G0044 G0033
G0022 D01 D02 D12 D10
D51 D53 D58 D82 H0215
R00326 1013; C999 C124
C113; S9999 S1456*R;
H0259; P1150; P1285;

Polymer Index [2.11]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D83
R00964 1145; G0055 G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D84
H0215 R00805 11179; C999
C124 C113; S9999
S1456*R; H0259; P1150;

Polymer Index [2.12]
018 ; H0022 H0011; G0044
G0033 G0022 D01 D02 D12
D10 D51 D53 D58 D83
R00964 1145; G0044 G0033
G0022 D01 D02 D12 D10
D51 D53 D58 D86 H0215
R02043 785; C999 C124
C113; S9999 S1456*R;
H0259; P1150;

Polymer Index [2.13]
018 ; ND01; Q9999 Q6917;
B9999 B4795 B4773 B4740;
B9999 B4955 B4944 B4922
B4740; B9999 B5221
B4740;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2000-102751